MECHANISMS OF FORMATION OF MAGNETITE IN MARTIAN METEORITE ALH84001.

J. P. Bradley[1], H. Y. McSween, Jr.[2], and R. P. Harvey[3]. [1] MVA Inc., 5500/200 Oakbrook Pkwy, Norcross, GA 30093, [2] Dept. of Geological Sciences, University of Tennessee, Knoxville, TN37996-1410; [3] Dept. of Geological Sciences, Case Western Reserve University, Cleveland, OH 44106-7216.

Magnetite is an important constituent within the carbonate-rich fracture zones of the ALH84001 meteorite. It is found within several distinct petrographic settings, including sulfide-rich and magnetite-rich bands (both on the outer rims of carbonates), in glass-rich veins within the carbonates, and as individual nanocrystals decorating the surfaces of carbonates [1-3]. Although the majority of the magnetite crystals in ALH84001 provide no specific information about their growth mechanism(s), transmission electron microscopy (TEM) studies have shown some crystals provide very specific information about mechanisms of crystal growth, as well as insight regarding the thermal histories of magnetite and other minerals within the fracture zones of the meteorite [2,3].

Two mechanisms of crystal growth have been identified among the nanophase magnetites, spiral growth about axial screw dislocations and epitaxial growth [2,3]. The spiral growth mechanism is found in magnetite whiskers which decorate the carbonates. The term “whisker” is restricted here to single crystals with unusual elongated morphologies resulting either from (1) anisotropy introduced into the structure during crystal growth, or (2) anisotopy in the crystal growth medium [4]. (Minerals that are naturally elongated and those formed by pseudomorphic replacement of elongated crystals are not considered whiskers).

Axial screw dislocations are an example of the first type of anisotropic crystal growth. Screw-dislocated whiskers of a wide variety of metals (Mn, Fe, Co, Ni, Cu, Zn) and refractory metal oxides (Al_2O_3,Fe_2O_3, CuO) have been synthesized by vapor phase condensation [5,6], and they are found in nature as condensates from high-temperature vapors and supercritical fluids [4,7,8]. Screw-dislocated whiskers of salts (e.g. NaCl, LiF, CdI_2) have been precipitated from aqueous solutions [9]. In principle, either vapor phase condensation or aqueous precipitation could have produced the magnetite whiskers in ALH84001, but vapor phase growth is the more likely because (a) ALH84001 is a conspicuously dry meteorite [10,11], (b) we are unaware of any reports of screw-dislocated magnetite whiskers precipitated from aqueous solutions, (c) screw-dislocated iron oxide whiskers have been synthesized from vapors in the laboratory [12], and (e) vapor deposited iron oxide whiskers (e.g. magnetite) are observed in nature [2,7].

The mechanism of spiral growth via screw dislocations was first proposed by Frank [13], who recognized that crystal growth from the vapor phase can occur at levels of supersaturation well below those expected for classical two-dimensional nucleation. According to the mechanism, an emergent screw dislocation on a crystal face provides a permanent, self-propagating growth step which allows one-dimensional (rather than two-dimensional) crystal growth to occur. One-dimensional nucleation significantly reduces the degree of supersaturation required for crystal growth. Observations of spiral ledges on the growth surfaces of crystals of many compounds and minerals confirm the Frank mechanism of spiral growth.

Some of the magnetite whiskers in ALH84001 appear to be free of axial screw dislocations, suggesting others mechanisms crystal growth. Simultaneous growth of whiskers by multiple mechanisms in the same environment is commonly observed in vapor phase syntheses and in nature, producing whiskers with and without screw-dislocations, whiskers with square, rectangular, or round cross-sections, and saw-toothed blades and ultrathin ribbons [2, 4, 7,14]. The coexistence of whiskers and other morphologies (e.g. platelets) that apparently grew by different mechanisms strongly suggests that it is the growth conditions (e.g. vapor composition, degree of supersaturation, temperature, pressure) rather than the specific mechanisms of whisker growth that determine whether whiskers or equant crystals grow from vapors and fluids. When conditions are appropriate, whiskers form by a variety of mechanisms.

The overwhelming majority of the magnetite nanocrystals in the fracture zones of ALH84001 are not whiskers (i.e. their morphologies are more equant), but often the overwhelming majority of crystals in vapor phase condensate deposits are not whiskers either [7]. For example, we observe that <1% of the vapor condensed crystals from two fumerole deposits are whiskers, while the rest are relatively equant crystals that provide no specific information about their mechanism(s) of growth. Thus, the presence of whiskers at any abundance within the fracture zones of ALH84001 should be viewed as a "fingerprint" of vapor phase growth.

Other magnetite nanocrystals within the fracture zones of ALH84001 are epitaxially intergrown with one another and the carbonate substrates upon which they are deposited [3]. Epitaxial growth can be viewed as an example of the second type of whisker growth, anisotropy in the crystal growth medium. Often these whiskers are found in groups or "schools" with similar orientations, i.e. they are aligned with their longest axes pointing in a common direction. Specimen tilting experiments, darkfield imaging, and selected area electron diffraction indicate that the crystals have similar crystallographic orientations and that their parallel orientations result from epitaxial nucleation and growth on carbonate. Similarly oriented "schools" of vapor-deposited whiskers (of multiple compositions) have been observed elsewhere [7,14,15]. We also observe platelets and other more equant magnetites epitaxially grown on the carbonates in ALH84001.

The mechanisms of whisker formation we have identified (spiral growth and epitaxy) provide insight about the thermal regime of magnetite growth in ALH84001. Although there is a vast literature on whisker growth phenomena in general, limited data exist on the formation of magnetite whiskers in particular. Vapor-deposited magnetite whiskers (some with axial features) recovered from the Merapi fumerole, Indonesia condensed at 600-800^{o} C [7]. Magnetite (and hematite) whiskers from fumeroles in the Valley of Ten Thousand Smokes, Alaska may have condensed (from halide vapors) at temperatures <500^{o} C [16]. (We are presently performing a detailed characterization of magnetites from both fumeroles using TEM). Spiral growth of massive (as opposed to whisker) magnetite has been observed in high-temperature metasomatic mineral deposits [17] and on the surfaces of steel etched with hydroxide solutions at 300^{o} C [18]. Epitaxial growth of magnetite crystals on carbonate was observed when chalybite ($FeCO_3$) single crystals were sealed under vacuum in tubes and heated under their own CO_2 pressure to 550^{o} C [19]. Although neither spiral growth or epitaxy is unique to vapor-phase growth, evidence of *both* mechanisms in ALH84001 is entirely consistent with vapor-phase whisker growth phenomena observed elsewhere in nature and laboratory syntheses.

Our magnetite data provide only limited insight regarding the formation temperature of the carbonates. Since they provided fresh surfaces for the nucleation and growth of magnetite, their formation was either concurrent with or immediately preceded magnetite formation. Carbonate formation may have preceded magnetite formation at significantly lower temperatures, although the carbonates would likely have been subsequently exposed to elevated temperatures during magnetite growth. Recent evidence that the carbonates have been shocked and intruded by shock melt also implies significant temperature excursions [20-21].

REFERENCES: [1] D. S. McKay *et al.* (1996) *Science* **273,** 924. [2] J. P. Bradley *et al. Geochim. Cosmochim. Acta* **60**, 475 (1996). [3] J. P. Bradley *et al.* (1997) *Met. Planet. Sci.* **32**, A20. [4] D. R. Veblen and J. E. Post (1983) *Am. Min.* **68**, 790. [5] E. M. Nadgornyi (1962) *Sov. Phys. Usp.* **5,** 462. [6] A. P. Levitt (1970) *Whisker Technology* (Wiley-Interscience, New York). [7] R. Symonds R. (1993) *Geochem. J.* **26**, 337. [8] J. P. Bradley *et al.* (1983) *Nature* **301,** 473. [9] S. Amelinckx (1958) *J. Appl. Phys.* **29**, 1610. [10] R. P. Harvey and H. Y. McSween Jr. (1996) *Nature* **382**, 49. [11] A. Trieman (1998) *Met. Planet. Sci.* (in press). [12] R. L. Tallman and E. A. Gulbransen (1968) Nature **218**, 1046. [13] F. C. Frank (1949) *Dis. Far. Soc.* **5**, 48. [14] Givargizov E. I. (1978) *Curr. Top. Mat. Sci.* **1,** 79. [15] F. Henriquez and R. F. Martin (1978) *Can. Min*. **16,** 581. [16] E. G. Zeis (1929) *Natl. Geog. Soc. Tech. Pap.* **1**(4), 1. [17] T. A. Velikoborets (1968) *Dokl. Akad. Nauk SSSR* **182**(1), 179. [18] O. Osai (1967) *Denki Kagaku* **35**(9) 638. [19] J. D. Bernal *et al* (1959) *Clay Min. Bull* **4**, 15. [20] G. A. McKay and G. E. Lofgren (1997) *Lunar planet. Sci.* **XXVIII,** 921. [21] E. R. D Scott *et al.* (1997) *Nature* **387**, 377.